Supporting information

Reusable Co-nanoparticles for general and selective Nalkylation of amines and ammonia with alcohols

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S1. Materials and methods

Alcohols and amines were obtained commercially from various chemical companies. Cobalt(II) nitrate hexahydrate (cat no.139267-100G) and silica suspension (Silica LUDOX® AS-40 colloidal silica, cat no. 420840-1L) were purchased from Sigma Aldrich. 1,10-Phenanthroline monohydrate (cat no. P0879-25G), 2, 2'-bipyridine (cat no. B0468 -25G) and 2,2':6',2"-terpyridine (cat no. T0024 -1G) were purchased from TCI Chemicals. 2,6-Bis(2-benzimidazolyl)pyridine (cat no. 379433-1G) was purchased from Sigma Aldrich. The pyrolysis experiments were carried out in Dekema Austromat 624 oven. All catalytic experiments were carried out in ACS pressure tubes. Unless otherwise stated all reagents were used directly without purification.

XRD powder pattern were recorded on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector using automatic divergence slits and Cu k α 1/ α 2 radiation (40 kV, 40 mA; λ = 0.15406 nm, 0.154443 nm). Cu beta-radiation was excluded using a nickel filter foil. The measurements were performed in 0.0167° steps and 100 s of data collecting time per step. The samples were mounted on silicon zero background holders. The obtained intensities were converted from automatic to fixed divergence slits (0.25°) for further analysis. Peak positions and profile were fitted with Pseudo-Voigt function using the High Score Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

The low-resolution imaging of catalyst morphology was obtained with a transmission electron microscope (TEM) JEOL equipped with a LaB6 emission gun and operating at 160 kV. Microscopic TEM images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-Energy Dispersive X-ray Spectroscopy (EDS) with acquisition time 20 min. For HRTEM analysis, the powder samples were dispersed in ethanol and 5 min ultrasonicated. One drop of this solution was placed on a copper grid with holey carbon film.

XPS surface investigation has been performed on the PHI 5000 Versa Probe II XPS system (Physical Electronics) with monochromatic Al-K α source (15 kV, 50 W) and photon energy of 1486.7 eV. Dual beam charge compensation was used for all measurements. All the spectra were measured in the vacuum of 1.3 x 10⁻⁷ Pa and at the room temperature of 21 °C. The analyzed area on each

sample was spot of 200 μ m in diameter. The survey spectra were measured with pass energy of 187.850 eV and electron volt step of 0.8 eV while for the high-resolution spectra was used pass energy of 23.500 eV and electron volt step of 0.2 eV. The spectra were evaluated with the MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the carbon peak C 1s at 284.80 eV.

GC and GC-MS analysis were recorded on Agilent 6890N instrument. GC conversion and yields were determined by GC-FID, HP6890 chromatograph with FID detector, column HP 530 m x 250 mm x 0.25 μ m. NMR spectra are recorded using Bruker 300 Fourier, Bruker AV 300 and Bruker AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, bs = broad singlet d = doublet, t = triplet and m = multiple. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra (CDCl₃: δ H = 7.26 ppm, δ C = 77.12 ppm; DMSO-d₆: δ H = 2.50 ppm, δ C = 39.52 ppm). High resolution mass spectra (HRMS) were obtained either from a MAT 95 XP from Thermo (EI) or from an HPLC system 1200 and downstream ESI-TOF-MS 6210 from Agilent (ESI).

S2 Procedure for the preparation of catalysts

In a 100 mL dried round bottomed flask, 291.03 mg Co(NO₃)₂·6H₂O (1 mmol) and 543.09 mg 1,10phenanthroline monohydrate (L1; 3 mmol,) were dissolved in 30 mL ethanol by stirring for 30 minutes at room temperature. To this solution, 1.25 g colloidal silica aqueous solution (Ludox HS-40, 40 wt%,) was added and continued stirring for 20 hours at 60 °C. Then, the reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation and dried under high vacuum. The obtained solid material (Co-L1-SiO₂, ~1168 mg, 88%) was grounded to a fine powder and transferred to crucible. The crucible was closed with a lid and placed in a pyrosis oven and then heated to the defined temperature (400, 600, 800, and 1000 °C) for 2 h at the heating rate of 5 °C/min under Argon gas. After the completion of pyrolysis, the oven was cooled down to room temperature and the material was removed from the oven (Co-L1/SiO₂-800, ~898 mg, 67%). Next, the obtained samples were etched in 5 M NH₄HF₂ aqueous solution at room temperature for 24 h to remove the SiO₂ template and larger particles. Finally, the resulting catalytic material was filtered and washed subsequently with deionized water and ethanol for three times and finally dried under vacuum (CoNC-L1@800, ~375 mg, 28.2%). The catalyst was named as Co-NC-L1@T (T represented the pyrolysis temperature). Elemental Analysis of optimal catalyst, Co-NC-L1@800: Co=1.7 wt%, C=78.1 wt%, N=3.72 wt%, H=0.79 wt%, Si=0.2 wt%). The same procedure was applied for the preparation of other catalysts using different ligands such as 2,2'-bipyridine (L2), 2,2';6',2"-terpyridine (L3), and 2,6-bis(2-benzimidazolyl)pyridine (L4).

<u>S3 Characterization of catalysts</u>

XRD patterns



Figure S1. XRD pattern of Co@NC-800-L1 catalyst.



Figure S2. XRD pattern of cobalt particles-800 catalyst (prepared without ligand).



Figure S3. XRD pattern of Co@NC-800-L1-R recycled catalyst.

<u>TEM images</u>



Figure S4. TEM images of Co@NC-800-L1-R recycled catalyst.



Figure S5. TEM images of cobalt particles-800 catalyst (prepared without ligand).

XPS spectra



Figure S6. High resolution X-ray photoelectron spectra (HR-XPS) for Co@NC-800-L1-R recycled catalyst. a) C1s, b) N1s, c) O1s and d) Co2p region.

S4. General procedure for the N-alkylation of amines with alcohols

S4.1 N-Alkylation of amines with alcohols

The magnetic stirring bar, 0.5 mmol amine and 1 mmol alcohol, 15 mg catalyst (Co-NC-L1@800 and 0.5 mmol t-BuOK were transferred to 20 mL pressure tube. Then, 2 mL dry toluene was added, and the pressure tube was flushed with argon and fitted with screw cap. The pressure tube containing reaction mixture was placed in aluminum block and reaction was allowed to progress under stirred condition at 140 °C for 24 h. After the completion of the reaction, the pressure tube was cooled to room temperature and the cap was slowly removed. Then, the reaction products were removed from the pressure tube, and the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding secondary amines were purified by column chromatography (silica; pentene-ethyl acetate mixture) and characterized by NMR, GCMS and HRMS spectral analysis. Following procedure is applied for determining the conversion and yield by GC: After completion of the reaction, n-hexadecane (50 µL) as standard was added to the reaction

pressure tube and the reaction products were diluted with ethyl acetate followed by filtration using plug of silica. Then the filtrate containing products were analyzed by GC.

	NH ₂ + OH Co@NC-800-L Toluene 140 °C, 24h			4
Entry	Catalyst	Conv. 1 (%)	Yield 3 (%)	Yield 4 (%)
1	Co@NC-800-L1	>99	99	-
2	Co@NC-800-L2	>99	96	5
3	Co@NC-800-L3	96	87	8
4	Co@NC-800-L4	90	81	8
5	Co@NC-400-L1	75	44	29
6	Co@NC-600-L1	93	80	10
7	Co@NC-1000-L1	>99	88	9
8	Co-particles-800 (without ligand)	84	56	27
9	Co@NC-800-L1-SiO ₂ (with SiO ₂)	67	43	21
10 ^[b]	Co@NC-800-L1 (without base)	86	57	27
11 ^[c]	1 equivalent of t-BuOK	21	15	5
12	Co(NO ₃) ₂ -L1-SiO ₂ (Unpyrolyzed)	23	17	5
13	Co(NO ₃) ₂ .6H ₂ O	30	23	6
14	Co(NO ₃) ₂ -L1	40	31	7
15	NC-800-L1 (without cobalt)	23	18	5

Table S1. N-Alkylation of aniline with benzyl alcohol: Testing of cobalt catalysts ^[a].

^[a] Reaction conditions: 0.5 mmol aniline, 1 mmol benzyl alcohol, 15 mg catalyst (0.86 mol% Co), 0.5 mmol t-BuOK (1 equiv.), 2 mL toluene, 140 °C, 24 h. For homogeneous catalysis conditions, 1 mmol cobalt nitrate and 3 mmol ligand were used. ^[b] Without base. ^[c] Without catalyst and in presence of 0.5 mmol t-BuOK (1 equiv.). Conversions and yields are based on aniline and determined by GC using n-hexadecane standard.

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Table S2. N-Alkylation of aniline with benzyl alcohol: Testing of different bases.

$ \underbrace{ \begin{array}{c} & NH_2 \\ + & & OH \end{array} }_{Toluene} \underbrace{ \begin{array}{c} Co@NC-800-L1 \\ Toluene \\ 140 \ ^{\circC. 24h} \end{array} }_{Toluene} \underbrace{ \begin{array}{c} H \\ H \\$						
Entry	Base	Conv. 1 (%)	Yield 3 (%)	Yield of 4 (%)		
1	Cs ₂ CO ₃ (1 equiv.)	62	55	6		
2	K ₃ PO ₄ (1 equiv.)	81	64	16		
3	K ₂ CO ₃ (1 equiv.)	57	23	22		
4	KOH (1 equiv.)	88	74	12		
5	t-BuOK (1 equiv.)	>99	99	-		
6	t-BuOK (0.1 equiv.))	43	28	14		
7	t-BuOK (0.2 equiv.))	80	67	11		
8	t-BuOK (0.5 equiv.)	88	74	12		
9	t-BuOK (0.75 equiv.)	96	88	7		

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Reaction conditions: 0.5 mmol aniline, 1 mmol benzyl alcohol, 20 mg catalyst (1.15 mol% Co), 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC using n-hexadecane standard. Table S3. N-Alkylation of aniline with benzyl alcohol: Testing of different solvents.

(H Co@NC-800-L1 Solvent 140 °C, 24h		
Entry	Solvent	Conv. 1 (%)	Yield 3 (%)	Yield of 4 (%)
1	o-Xylene	90	78	11
2	p-Xylene	89	72	15
3	THF	97	86	12
4	MeCN	54	43	9
5	Toluene	>99	99	-
6	Dioxane	91	80	10

Reaction conditions: 0.5 mmol aniline, 1 mmol benzyl alcohol, 20 mg catalyst (1.15 mol% Co), 2 mL 0.5 mmol, t-BuOK solvent, 140 °C, 24 h. Conversion and yields are based on aniline and determined by GC using n-hexadecane as standard.

 Table S4. N-Alkylation of aniline with benzyl alcohol: Testing of different benzyl alcohol

 amount.



Entry	Benzyl alcohol	Conv. 1	Yield 3 (%)	Yield of 4 (%)
	amount	(%)		
1	0.5 mmol (1 equiv.)	88	62	25
2	0.7 mmol (1.4 equiv.)	>99	93	5
3	1.0 mmol (2 equiv.)	>99	99	-

Reaction conditions: 0.5 mmol aniline, 20 mg catalyst (1.15 mol% Co), 0.5 mmol t-BuOK, 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC using n-hexadecane standard.

Entry	Catalyst	Reaction	Yield. %	Sel. %	Catalyst loading	Ref.
		conditions				
1	Co@NC-	140 °C, 24 h,	99%	99%	0.86 mol% Co	this work
	800-L1					
2	Pd@SiO ₂	150 °C, 30 h	97%		1 mol% Pd	(22a)
3	Pd/MgO	180 °C, 0.25 h.	79%	80%	0.8% Pd	(22b)
4	Ni/CaSiO ₃	155 °C, 17 h	78%	78%	2 mol% Ni	(23a)
5	Ni/θ-Al ₂ O ₃	144 °C, 3 h	99%	99%	1 mol% Ni	(23b)
6	Ni/Al ₂ O ₃	150 °C, 72 h	78%	79%	5 mol% Ni	(24)
7	15Ni/Al-β-CD	140 °C, 1 h	38%	64%	35 mg	(25)
8	Ni(COD) ₂	140 °C, 18 h	99%	99%	3 mol%	(26)
9	NiCuFeOx	Reflux in xylene		94%	50 mg (>30	(27)
		solvent, 24 h			mol% of Ni+Cu)	
10	Cu@ Mg-Al	180 °C, 15 h	98%	98%		(30)
	hydrotalcite					
11	Copper	160 °C, 24 h	99%	99%	3 mol% Cu	(32)
	Powder					

 Table S5. Comparison of activities of our Co-catalyst with previously reported heterogeneous catalysts.





Reaction conditions: 0.5 mmol aniline, 1 mmol benzyl alcohol, 15 mg catalyst, 0.5 mmol t-BuOK, 2 mL toluene, 140 °C, 24 h. Conversions and yields are based on aniline and determined by GC using n-hexadecane standard.

S4.2 Methylation of anilines

The magnetic stirring bar, 0.5 mmol aniline, 50 mg Co-NC-L1@800 and 1 mmol t-BuOK were transferred to 20 mL pressure tube and 2 mL methanol was added. Then, the pressure tube was flushed with argon and closed with screw cap. The pressure tube containing reaction mixture was placed into aluminum block and allowed to progress at 160 °C for desired time. After the completion of the reaction, the pressure tube was cooled to room temperature. Then, the samples were removed from pressure tube, and the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding N-methylated products were purified by column chromatography (silica; pentene-ethyl acetate mixture) and characterized by NMR and HRMS spectral analysis.

S4.3 Synthesis of primary amines using alcohols and ammonia.

The magnetic stirring bar, 0.5 mmol corresponding alcohol, 30 mg Co-NC-L1@800 and 0.5 mmol t-BuOK were transferred to 8 mL glass vial and then 2 mL dry toluene was added. Then, the vial was fitted with septum, cap and needle. The reaction vials (8 reactions vials at a time containing different substrates) were placed into a 300 mL autoclave. The autoclave was flushed with 20 bar of nitrogen 2 times and then it was pressurized to 5-7 bar ammonia. The autoclave was placed into an aluminum block preheated at 150 °C and the reactions were stirred for required time. After the completion of the reactions, the autoclave was cooled to room temperature. The remaining ammonia was discharged, and the samples were removed from the autoclave. The solid catalyst was filtered off and washed thoroughly with ethyl acetate. The reaction products were analyzed by GC-MS. The corresponding amines were purified by column chromatography (silica; n-hexane-ethyl acetate mixture) and characterized by NMR and HRMS spectral analysis. For conversion into hydrochloride salt of amine, 1-2 mL methanolic HCl (1.5M HCl in methanol) was added to the ether solution of respective amine and stirred at room temperature for 4-5 h. Then, the solvent was removed, and the resulted hydrochloride salt of amine is dried under high vacuum.

S5 Catalyst recycling

The magnetic stirring bar, 1 mmol aniline and 2 mmol benzyl alcohol, 30 mg Co-NC-L1@800 and 1 mmol t-BuOK were transferred to 20 mL pressure tube and 3 mL dry toluene was added. The pressure tube was flushed with argon and closed with screw cap. Then, it was placed into an aluminum block and heated to 140 °C for desired time. After the completion of the reaction, the pressure tube was cooled down to room temperature. To the reaction products, 100 μ L n-hexadecane as standard was added. The catalyst was separated by centrifugation and the centrifugate containing reaction products was subjected to GC analysis. The separated catalyst was washed with water, methanol and ethyl acetate and then dried under vacuum. The dried catalyst was used for the next run without further purification or reactivation.

S6 NMR and HRMS data

NOTE: For some compounds intensity of -NH peak is very low and hence not properly visible in ¹H-NMR.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.41-7.27 (m, 5H), 7.23 – 7.16 (m, 2H), 6.80 – 6.74 (m, 1H), 6.66 – 6.73 (m, 2H), 5.12 (bs, 1H), 4.32 (s, 2H).

¹³C NMR (75 MHz, Chloroform-d) δ 138.6, 129.3, 128.6, 127.8, 127.4, 118.5, 113.7, 48.9. HRMS (ESI): Calculated for $C_{13}H_{13}N$ [M+H] = 184.1126; found = 184.1126.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 1H), 7.18 – 7.10 (m, 4H), 7.10 – 7.06 (m, 1H), 6.70 – 6.61 (m, 1H), 6.59 – 6.52 (m, 2H), 4.21 (s, 2H), 3.75 (bs, 1H), 2.23 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 148.3, 137.1, 136.4, 130.5, 129.3, 128.3, 127.5, 126.3, 117.5, 112.8, 46.5, 19.1. HRMS (ESI): Calculated for C₁₄H₁₅N [M+H] = 198.1283; found = 198.1278.

Yield of product 5: 85%; 84.0 mg, 0.424 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.21 – 7.15 (m, 2H), 6.75 – 6.70 (m, 1H), 6.69 – 6.63 (m, 2H), 4.29 (s, 2H), 1.33 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 150.3, 148.2, 136.3, 129.7, 129.3, 127.4, 126.0, 125.6, 117.6, 112.2, 48.1, 31.4, 31.1.

HRMS (EI): Calculated for $C_{17}H_{21}N = 240.1752$; found = 240.1750.

Yield of product 7: 84%; 101 mg, 0.42 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.57 (m, 4H), 7.50 – 7.43 (m, 4H), 7.40 – 7.34 (m, 1H), 7.25 – 7.19 (tt, *J* = 1.0, 7.4, 2H), 6.80 – 6.74 (td, *J* = 1.1, 7.3, 1H), 6.72 – 6.67 (m, 2H), 4.38 (s, 2H), 4.25 (bs, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.0, 140.9, 140.3, 138.4, 129.3, 128.8, 127.9, 127.4, 127.3, 127.1, 117.7, 113.0, 48.1.

HRMS (EI): Calculated for $C_{19}H_{17}N = 259.1355$; found = 259.1357.

Yield of product 8: 86%; 112 mg, 0.43 mmol.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.19 – 6.99 (m, 4H), 6.88 (t, *J* = 4.3 Hz, 2H), 6.59 (dd, *J* = 7.9, 6.7 Hz, 1H), 6.53 – 6.43 (m, 2H), 4.15 (s, 2H), 3.84 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-d) δ 163.7, 147.9, 135.2, 135.1, 129.3, 129.1, 128.9, 117.7, 115.6, 115.5, 115.3, 115.2, 112.9, 47.6.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -125.77.

HRMS (ESI): Calculated for $C_{13}H_{12}NF[M+H] = 201.1073$; found = 201.1071.

Yield of product 9: 82%; 82.4 mg, 0.41 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 2H), 7.17 – 7.05 (m, 5H), 6.67 – 6.62 (tt, *J* = 1.1, 7.3, 1H), 6.56 – 6.52 (m, 2H), 4.35 (s, 2H), 4.11 (bs, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.7, 136.7, 133.2, 129.5, 129.3, 129.1, 128.4, 126.9, 117.8, 112.9, 45.9.

HRMS (ESI): Calculated for $C_{14}H_{12}NC1$ [M+H] = 218.0736; found = 218.0736. Yield of product 10: 84%; 91.6 mg, 0.42 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.14 – 7.03 (m, 2H), 6.99 – 6.82 (m, 2H), 6.76 – 6.63 (m, 1H), 6.53 – 6.44 (m, 2H), 4.20 (s, 2H), 4.09 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 153.1, 152.9, 149.8, 149.6, 147.2, 140.3, 136.2, 129.4, 118.3, 112.9, 110.9, 110.8, 110.7, 110.6, 47.1.

¹⁹F NMR (282 MHz, Chloroform-d) δ -137.83, -167.15.

HRMS (ESI): Calculated for $C_{14}H_{10}NF_3[M+H] = 238.0843$; found = 238.0848.

Yield of product 11: 87%; 103.6 mg, 0.435 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.63 – 7.46 (m, 4H), 7.25 – 7.12 (m, 2H), 6.79 – 6.71 (m, 1H), 6.66 – 6.58 (m, 2H), 4.42 (s, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 162.4, 139.7, 136.4, 130.2, 122.6, 32.3, 20.8.

 ^{19}F NMR (282 MHz, Chloroform-d) δ -62.47.

HRMS (ESI): Calculated for $C_{14}H_{12}NF_3$ [M+H] = 252.1000; found = 252.1004.

Yield of product 12: 80%; 101 mg, 0.40 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 1H), 7.56 – 7.48 (dd, *J* = 7.9, 15.6, 2H), 7.45 – 7.40 (m, 1H), 7.18 – 7.13 (m, 2H), 6.79 – 6.68 (m, 1H), 6.64 – 6.56 (m, 2H), 4.35 (s, 2H), 4.31 (bs, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.5, 140.4, 130.7, 129.3, 129.3, 129.2, 129.1, 124.2, 124.1, 124.1, 120.8, 118.2, 113.1, 48.0.

 ^{19}F NMR (282 MHz, Chloroform-d) δ -62.66.

HRMS (ESI): Calculated for $C_{14}H_{12}NF_3$ [M+H] = 252.1000; found = 252.1003.

Yield of product 13: 82%; 103.4 mg, 0.41 mmol.



¹H NMR (300 MHz, DMSO- d_6) δ 7.45 – 7.44 (d, J = 0.6, 2H), 7.43 – 7.42 (t, J = 0.8, 2H), 7.41 – 7.40 (m, 3H), 7.25 – 7.23 (q, J = 1.4, 2H), 7.01 – 6.94 (m, 2H), 6.77 – 6.72 (m, 1H), 6.69 – 6.65 (m, 2H), 6.16 (bs, 1H), 5.15 (s, 2H), 4.21 (s, 2H).

¹³C NMR (101 MHz, DMSO-d6) δ 157.6, 149.1, 137.6, 132.7, 129.2, 128.9, 128.8, 128.2, 128.1, 116.1, 115.1, 112.8, 69.6, 46.4.

HRMS (EI): Calculated for $C_{21}H_{23}ON = 306.1571$; found = 306.1569.

Yield of product 14: 85%; 130.1 mg, 0.425 mmol.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.22 – 7.16 (m, 2H), 7.12 – 7.03 (m, 2H), 6.81 – 6.74 (m, 2H), 6.65 – 6.58 (m, 1H), 6.57 – 6.51 (m, 2H), 4.15 (s, 2H), 3.92 (bs, 1H), 3.66 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 158.9, 148.1, 131.3, 129.2, 128.8, 117.6, 114.0, 112.9, 55.3, 47.8.

HRMS (ESI): Calculated for $C_{14}H_{15}NO [M+H] = 214.1232$; found =214.1232. Yield of product 15: 88%; 94.2 mg, 0.44 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 – 7.15 (m, 2H), 6.67 – 6.65 (dd, J = 0.9, 2.1, 2H), 6.64 – 6.60 (m, 3H), 4.25 (s, 2H), 3.83 (s, 9H), 3.56 (bs, 1H). ¹³C NMR (75 MHz,) δ 153.4, 148.2, 137.0, 135.2, 129.2, 117.7, 112.9, 104.3, 60.8, 56.1, 48.7. HRMS (EI): Calculated for C₁₆H₁₉NO₃ = 273.1359; found = 273.1357. Yield of product 17: 81%; 110.5 mg, 0.405 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 2H), 7.05–6.98 (dd, *J* = 0.6, 8.5, 1H), 6.71 – 6.61 (m, 4H), 4.30 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.84 (s, 3H).

¹³C NMR (75 MHz, Chloroform-d) δ 153.1, 151.9, 148.3, 142.2, 129.2, 125.1, 123.4, 117.4, 113.0, 107.2, 61.1, 60.8, 56.0, 43.2.

HRMS (EI): Calculated for $C_{16}H_{19}NO_3 = 273.1359$; found =273.1356.

Yield of product 18: 80%; 108.9 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.12 – 7.00 (m, 2H), 6.88 – 6.80 (m, 1H), 6.77 – 6.56 (m, 3H), 6.54 – 6.47 (m, 2H), 4.74 (bs, 1H), 4.09 (s, 2H), 3.71 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 148.2, 145.8, 145.8, 132.7, 129.3, 119.1, 117.5, 113.9, 112.9, 110.8, 56.0, 47.9.

HRMS (EI): Calculated for $C_{14}H_{15}NO_2 = 229.1097$; found = 229.1093.

Yield of product 19: 80%; 91.6 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.21 – 7.17 (m, 2H), 7.15 – 7.11 (m, 2H), 7.11 – 7.03 (m, 2H), 6.66 – 6.58 (m, 1H), 6.55 – 6.50 (m, 2H), 4.16 (s, 2H), 4.06 (bs, 1H), 2.35 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 147.8, 137.2, 136.3, 130.0, 129.3, 128.1, 127.0, 125.2, 117.8, 113.0, 47.9, 16.1. HRMS (EI): Calculated for $C_{14}H_{15}NS = 229.0903$; found = 229.0902.

Yield of product 20: 87%; 99.6 mg, 0.435 mmol.

¹H NMR (300 MHz, Chloroform-*d*) δ 8.15 – 8.05 (m, 2H), 7.54 – 7.38 (m, 2H), 7.14 – 7.03 (m, 2H), 6.74 – 6.61 (m, 1H), 6.56 – 6.46 (m, 2H), 4.39 (s, 2H), 4.25 (bs, 1H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 147.4, 147.2, 147.2, 129.4, 127.7, 123.9, 118.3, 113.0, 47.7. HRMS (EI): Calculated for C₁₃H₁₂N₂O₂ = 229.1934; found =229.1936. Yield of product 11: 77%; 88.2 mg, 0.385 mmol.

H N N

¹H NMR (300 MHz, Chloroform-d) δ 8.77 – 8.41 (m, 1H), 7.68 – 7.60 (td, J = 1.8, 7.7, 1H), 7.38 – 7.30 (dt, J = 1.0, 7.8, 1H), 7.22 – 7.14 (m, 3H), 6.77 – 6.70 (m, 1H), 6.70 – 6.65 (m, 2H), 4.51 (bs, 1H), 4.45 (s, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ158.5, 149.1, 147.9, 136.8, 129.3, 122.1, 121.6, 117.6, 113.1, 49.2.

HRMS (ESI): Calculated for $C_{12}H_{12}N_2$ [M+H] = 185.1078; found = 185.1081. Yield of product 24: 81%; 74.9 mg, 0.405 mmol.



¹H NMR (300 MHz, Chloroform-d) δ 8.76 – 8.48 (m, 2H), 7.76 – 7.58 (m, 1H), 7.32 – 7.05 (m, 3H), 6.80 – 6.70 (tt, *J*=1.1, 7.5, 1H), 6.67 – 6.51 (m, 2H), 4.33 (s, 2H), 3.99 (bs,1 H).

¹³C NMR (75 MHz, Chloroform-d) δ 149.1, 148.6, 147.6, 135.1, 134.9, 129.4, 123.6, 118.0, 112.9, 45.7.

HRMS (ESI): Calculated for $C_{12}H_{12}N_2$ [M+H] =185.1091; found =185.1090.

Yield of product 25: 85%; 78.7 mg, 0.425 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 1H), 7.31 – 7.33 (m, 2H), 7.25 – 7.22 (m, 3H), 6.47 (dd, J = 3.3, 0.7 Hz, 1H), 6.26 (dd, J = 3.3, 1.8 Hz, 1H), 4.85 (bs, 1H), 4.43 (s, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 143.6, 142.8, 129.6, 129.4, 121.1, 110.8, 110.5, 99.7, 46.3. HRMS (EI): Calculated for $C_{13}H_{11}NO = 174.1150$; found = 174.1149. Yield of product 26: 82%; 71.4 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.18 (m, 3H), 7.03 – 6.96 (m, 2H), 6.81 – 6.74 (tt, *J* = 1.1, 7.3, 1H), 6.73 – 6.66 (m, 2H), 4.51 (s, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 129.3, 129.2, 126.9, 125.2, 124.7, 124.1, 118.4, 113.5, 43.7. HRMS (EI): Calculated for C₁₁H₁₁NS = 189.0606; found = 189.0601.

Yield of product 27: 89%; 84.1 mg, 0.445 mmol.



¹H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.24 (tt, *J* = 1.0, 7.3, 2H), 7.10 – 7.02 (m, 2H), 6.84 – 6.78 (q, *J* = 1.1, 7.3, 1H), 6.76 – 6.68 (m, 3H), 6.59 – 6.54 (dd, *J* = 1.3, 8.4, 1H), 3.86 (s, 2H), 3.66 – 3.54 (m, 1H), 3.35 – 3.19 (m, 2H), 2.99 – 2.78 (m, 2H), 2.14 – 1.99 (m, 1H), 1.90 – 1.77 (m, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 148.3, 144.3, 129.4, 129.4, 126.9, 121.4, 117.9, 117.5, 114.5, 113.1, 50.7, 49.7, 26.2.

HRMS (EI): Calculated for $C_{16}H_{18}N_2 = 238.1464$; found = 238.1459.

Yield of product 28: 74%; 88.1 mg, 0.37 mmol.



¹H NMR (300 MHz, CDCl3) δ 7.25 – 7.16 (m, 2H), 6.92 – 6.71 (m, 4H), 6.69 – 6.62 (m, 2H), 5.98 – 5.94 (s, 2H), 4.26 – 4.24 (d, J = 0.7 Hz, 2H), 4.16 – 3.87 (s, 1H).

¹³C NMR (75 MHz, Chloroform-d) δ 148.0, 147.9, 146.7, 133.3, 129.3, 120.6, 117.6, 112.9, 108.3, 108.1, 101.0, 48.1.

HRMS (EI): Calculated for $C_{21}H_{23}ON = 229.0943$; found = 227.0941.

Yield of product 29: 82%; 93.8 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.20 – 6.36 (m, 8H), 4.16 – 4.04 (m, 6H), 3.05 (bs, 1H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 147.1, 131.9, 131.7, 128.2, 119.4, 116.4, 116.3, 115.8, 115.3, 111.7, 63.3, 63.3, 46.6.

HRMS (EI): Calculated for $C_{15}H_{15}NO_2 = 242.1040$; found = 242.1044.

Yield of product 30: 80%; 96.8 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.17 (m, 2H), 6.96 – 6.89 (m, 2H), 6.78 – 6.72 (m, 1H), 6.70 – 6.63 (m, 2H), 4.29 – 4.21 (s, 2H), 3.92 – 3.87 (m, 4H), 3.21 – 3.14 (m, 4H).

¹³C NMR (75 MHz, Chloroform-d) δ 150.6, 148.3, 130.8, 129.3, 128.6, 117.5, 115.9, 112.9, 66.9, 49.5, 47.8.

HRMS (EI): Calculated for $C_{17}H_{20}N_2O = 268.1570$; found = 268.1568.

Yield of product 31: 81%; 108.6 mg, 0.405 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.64 – 7.54 (m, 1H), 7.25 – 7.13 (m, 6H), 6.79 – 6.64 (m, 6H), 4.44 (s, 4H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 158.1, 147.9, 137.3, 129.3, 119.9, 117.7, 113.1, 49.3.

HRMS (EI): Calculated for $C_{19}H_{19}N_3 = 289.1574$; found = 289.1573.

Yield of product 32: 87%; 125.7 mg, 0.435 mmol.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 (tt, *J*=1.0, 7.4, 2H), 6.75 (tq, *J*=1.1, 7.2, 1H), 6.66 (dq, *J*=1.0, 7.6, 2H), 3.60 (bs, 1H), 3.15 (td, *J*=0.8, 7.1, 2H), 1.76 – 1.58 (m, 2H), 1.56 – 1.40 (m, 2H), 1.10 – 0.97 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.6,129.3, 117.1, 112.7, 43.7, 31.7, 20.4, 14.0.

HRMS (ESI): Calculated for $C_{10}H_{15}N$ [M+H] = 150.1283; found = 150.1283.

Yield of product 33: 65%; 48.8 mg, 0.325 mmol.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.23 – 7.10 (m, 5H), 3.88 (bs, 1H), 3.70 – 3.41 (m, 2H), 1.48 – 1.31 (m, 2H), 1.23 – 1.06 (m, 8H), 0.92 – 0.61 (m, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 138.9, 127.6, 126.9, 125.5, 52.1, 47.6, 30.6, 27.9, 26.0, 21.4, 12.9.

HRMS (ESI): Calculated for $C_{13}H_{21}N$ [M+H] = 192.1752; found = 192.1751.

Yield of product 34: 73%; 70.1 mg, 0.365 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.14 (m, 2H), 6.73 (t, *J* = 7.3, 1H), 6.68 – 6.63 (m, 2H), 4.08 (bs, 1H), 3.16 – 3.06 (m, 2H), 1.63 (dd, *J* = 6.7, 8.4, 2H), 1.30 – 1.26 (m, 12H), 0.90 – 0.87 (m, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 147.9, 129.2, 117.6, 113.2, 44.4, 31.8, 29.5, 29.4, 29.4, 29.3, 27.1, 22.6, 14.1.

HRMS (ESI): Calculated for $C_{15}H_{25}N$ [M+H] = 220.2065; found = 220.2066.

Yield of product 35: 75%; 82.5 mg, 0.375 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 2H), 6.70 (tt, *J* = 1.1, 7.3, 1H), 6.65 – 6.59 (m, 2H), 3.13 (d, *J* = 7.3, 2H), 2.60 (hept, *J* = 7.6, 1H), 2.19 – 2.07 (m, 2H), 1.99 – 1.87 (m, 2H), 1.80 – 1.71 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.4, 129.2, 117.3, 112.8, 49.9, 34.9, 26.1, 18.5. HRMS (ESI): Calculated for C₁₁H₁₅N [M+H] = 162.1283; found =162.1287.

Yield of product 36: 87%; 70.5 mg, 0.435 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dd, J = 8.6, 7.3 Hz, 2H), 6.69 (tt, J = 7.3, 1.1 Hz, 1H), 6.62 (dt, J = 7.7, 1.1 Hz, 2H), 3.27 (s, 1H), 2.96 (d, J = 6.6 Hz, 2H), 1.87 – 1.80 (m, 2H), 1.78 – 1.53 (m, 4H), 1.28 (d, J = 2.8 Hz, 1H), 1.27 – 1.20 (m, 2H), 1.05 – 0.94 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.5, 129.2, 117.0, 112.9, 112.7, 50.7, 37.5, 31.3, 26.6, 26.0. HRMS (EI): Calculated for C₁₃H₁₉N = 189.1512; found = 189.1514.

Yield of product 37: 80%; 75.6 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-d) δ 7.24 – 7.17 (m, 2H), 6.75 – 6.69 (dt, *J* = 1.1, 7.4 Hz, 1H), 6.67 – 6.61 (m, 2H), 5.79 – 5.57 (m, 2H), 3.95 – 3.39 (bs, 1H), 3.11 – 3.04 (d, *J* = 6.5 Hz, 2H), 2.30 – 2.06 (m, 3H), 2.01 – 1.74 (m, 3H), 1.44 – 1.30 (m, 1H).

¹³C NMR (75 MHz, Chloroform-d) δ 148.5, 129.2, 127.2, 125.9, 117.1, 112.7, 49.7, 33.5, 29.7, 26.8, 24.7.

HRMS (ESI): Calculated for $C_{13}H_{17}N$ [M+H] = 188.1439; found = 188.1444.

Yield of product 38: 78%; 103.4 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 2H), 6.78 (ddt, J = 1.1, 7.3, 8.4, 1H), 6.72 – 6.65 (m, 2H), 6.02 (ddt, J = 17.2, 10.3, 5.4 Hz, 1H), 5.35 (dq, J = 1.7, 17.2, 1H), 5.22 (dq, J = 1.5, 10.3, 1H), 3.82 (dt, J = 1.6, 5.4, 2H), 3.74 (bs, 1H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 148.0, 135.5, 129.3, 117.6, 116.3, 113.1, 46.6.

HRMS (EI): Calculated for $C_9H_{11}N = 134.0115$; found = 134.0113.

Yield of product 39: 45%; 30.15 mg, 0.225 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.23 (m, 1H), 7.18 – 7.09 (m, 4H), 6.70 – 6.64 (tt, *J* = 1.1, 7.4, 1H), 6.62 – 6.57 (m, 2H), 4.14 (s, 2H), 1.24 – 1.19 (m, 8H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.2, 148.0, 136.7, 129.3, 127.7, 126.7, 117.5, 112.9, 108.2, 48.1, 33.8, 31.5, 31.3, 24.1.

HRMS (EI): Calculated for $C_{16}H_{21}N = 227.1512$; found = 227.1515.

Yield of product 40: 77%; 87.4 mg, 0.385 mmol.



¹H NMR (300 MHz, Chloroform-d) δ 7.38 – 7.25 (m, 4H), 7.24 – 7.16 (m, 1H), 7.12 – 7.03 (m, 2H), 6.67 – 6.58 (m, 1H), 6.53 – 6.45 (m, 2H), 4.46 (q, *J* =6.7, 1H), 4.03 (bs, 1H), 1.49 (d, *J* =6.7, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 147.2, 145.2, 129.1, 128.7, 126.9, 125.9, 117.3, 113.3, 53.5, 25.1.

HRMS (EI): Calculated for $C_{14}H_{15}N = 198.1460$; found = 198.1458.

Yield of product 41: 84%; 83.1 mg, 0.42 mmol.

1H NMR (300 MHz, Chloroform-d) δ 7.26 – 7.03 (m, 6H), 6.67 (t, *J* =1.1, 7.4, 1H), 6.55 (d, 2H), 4.45 (q, *J* =6.7, 1H), 4.11 (bs, 1H), 2.33 (s, 3H), 1.52 (d, *J* =6.8, 3H).

¹³C NMR (75 MHz, Chloroform-d) δ 147.3, 142.2, 138.2, 129.1, 128.5, 127.7, 126.6, 122.9, 117.3, 113.3, 53.6, 25.0, 21.5.

HRMS (EI): Calculated for $C_{15}H_{17}N = 212.3198$; found = 212.3197.

Yield of product 42: 85%; 90.2 mg, 0.425 mmol.

H O

¹H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 2H), 7.30 – 7.24 (m, 2H), 7.05 – 6.98 (m, 2H), 6.87 (tt, *J* =1.1, 7.5, 1H), 6.83 – 6.77 (m, 2H), 3.96 (s, 3H), 3.93 – 3.84 (m, 1H), 3.69 (bs, 1H), 1.30 (d, *J* =6.4, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 158.2, 147.3, 130.5, 130.5, 129.4, 117.2, 113.8, 113.4, 55.2, 49.4, 20.2.

HRMS (EI): Calculated for $C_{15}H_{17}NO = 290.0716$; found = 290.0714.

Yield of product 43: 78%; 113.1 mg, 0.39 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 4.8, 2H), 7.37 – 7.28 (m, 2H), 7.16 – 7.03 (m, 2H), 6.78 – 6.64 (m, 1H), 6.52 – 6.39 (m, 2H), 4.46 (q, *J* = 6.8, 1H), 4.02 (bs, 1H), 1.52 (d, *J* = 6.8, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 154.6, 150.1, 146.6, 129.2, 121.3, 117.8, 113.2, 52.7, 24.5. HRMS (EI): Calculated for C₁₄H₁₈N₂ = 215.1239; found = 215.1237. Viold of product 44: 80%: 85.9 mg, 0.40 mmol

Yield of product 44: 80%; 85.9 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-d) δ 7.18 (td, *J* =2.0, 7.1, 2H), 6.81 – 6.55 (m, 3H), 3.50 (bs, 1H), 3.30 (tq, *J* =3.1, 3.7, 10.0, 1H), 2.10 (dp, *J* =2.7, 3.8, 12.2, 2H), 1.71 (ddq, *J* =3.9, 12.3, 32.2, 3H), 1.53 – 1.10 (m, 5H).

¹³C NMR (101 MHz, Chloroform-d) δ 147.4, 129.3, 116.9, 113.2, 51.7, 33.5, 26.0, 25.1. HRMS (EI): Calculated for C₁₂H₁₇N = 176.0146; found =176.0143.

Yield of product 46: 75%; 66.0 mg, 0.375 mmol.



¹H NMR (300 MHz, DMSO-d₆) δ 9.02 (s, 1H), 7.03 (ddd, *J* =0.9, 2.7, 8.5, 3H), 6.53 – 6.43 (m, 5H), 3.57 – 3.49 (m, 2H), 2.78 – 2.66 (m, 5H), 1.64 – 1.53 (m, 2H), 1.48 – 1.06 (m, 9H), 0.81 (s, 3H). ¹³C NMR (75 MHz, DMSO-d₆) δ 155.5, 155.3, 137.6, 130.9, 130.3, 126.4, 115.4, 115.3, 113.2, 113.1, 80.5, 49.9, 47.8, 44.0, 43.2, 37.0, 30.3, 29.6, 27.4, 26.5, 23.2, 13.9, 11.7. HRMS (EI): Calculated for C₂₄H₂₉NO = 348.0579; found = 348.0573. Yield of product 47: 60%; 104.3 mg, 0.30 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 8.40 – 8.17 (dd, J = 0.6, 4.7, 2H), 6.94 – 6.81 (t, J = 1.0, 1H), 6.82 – 6.66 (t, J = 0.7, 2H), 6.53 – 6.35 (td, J = 0.7, 4.7, 1H), 5.91 (s, 2H), 3.84 – 3.71 (m, 4H), 3.43 (s, 2H), 2.54 – 2.31 (m, 4H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 161.6, 157.6, 147.7, 146.7, 131.8, 122.2, 109.7, 109.5, 107.9, 100.9, 62.8, 52.8, 43.6.

HRMS (ESI): Calculated for $C_{16}H_{18}N_4O_2$ [M+H] = 299.1508; found = 299.1508. Yield of product 48: 90%; 134.5 mg, 0.45 mmol.



1 H NMR (300 MHz, DMSO-d6) δ 7.39 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 4.25 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.64 – 3.14 (m, 8H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.4, 153.1, 141.7, 128.5, 114.4, 108.2, 61.7, 60.9, 56.4, 47.3, 40.2.

HRMS (EI): Calculated for $C_{14}H_{22}N_2O_3 = 267.1045$; found = 267.1043.

Yield of product 49: 81%; 108.1 mg, 0.405 mmol.



¹H NMR (300 MHz, CDCl3) δ 7.31 – 7.21 (m, 7H), 7.20 – 7.11 (m, 6H), 4.25 – 4.05 (s, 1H), 3.45 – 3.39 (s, 2H), 2.50 – 2.11 (s, 8H), 1.25 – 1.23 (s, 9H).

¹³C NMR (75 MHz, Chloroform-d) δ 149.9, 142.2, 141.5, 134.8, 132.5, 129.2, 129.0, 128.6, 127.9, 127.1, 125.5, 125.1, 75.4, 62.7, 53.3, 51.8, 34.4, 31.4.

HRMS (EI): Calculated for $C_{28}H_{33}N_2Cl = 434.1122$; found = 434.1120.

Yield of product 50: 82%; 177.9 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.45 – 7.27 (m, 5H), 7.07 – 6.99 (m, 2H), 6.65 – 6.57 (m, 2H), 4.30 (s, 2H), 3.90 (bs, 1H), 2.29 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 145.9, 139.6, 129.8, 128.6, 127.5, 127.2, 126.8, 113.1, 48.7, 20.4.

HRMS (EI): Calculated for $C_{14}H_{15}N = 198.0319$; found = 198.0317.

Yield of product 51: 84%; 83.1 mg, 0.42 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.44 – 7.25 (m, 5H), 7.14 – 7.07 (m, 1H), 6.60 (t, *J* =0.8, 1H), 6.54 – 6.46 (m, 2H), 4.33 (s, 2H), 4.03 (bs, 1H), 2.33 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 148.2, 139.5, 139.1, 129.2, 128.7, 127.6, 127.2, 118.6, 113.7, 110.0, 48.4, 21.7.

HRMS (EI): Calculated for $C_{14}H_{15}N = 198.2846$; found = 198.2844.

Yield of product 52: 80%; 79.3 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 5H), 7.08 (m, 1H), 6.24 (s, 1H), 6.16 (s, 2H), 4.59 (bs, 1H), 4.15 (s, 2H), 2.07 (s, 6H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 148.3, 139.6, 138.9, 128.6, 127.5, 127.1, 119.5, 110.7, 48.3, 21.5.

HRMS (ESI): Calculated for $C_{15}H_{17}N$ [M+H] = 212.1439; found = 212.1442.

Yield of product 53: 86%; 91.2 mg, 0.43 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 5H), 6.83 – 6.68 (m, 2H), 4.05 – 4.00 (m, 2H), 2.16 (s, 9H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 140.5, 131.8, 130.2, 129.6, 129.3, 128.9, 128.6, 128.2, 128.1, 127.3, 53.3, 20.7, 18.3.

HRMS (ESI): Calculated for $C_{16}H_{19}N$ [M+H] = 226.1595; found = 226.1595.

Yield of product 54: 73%; 82.5 mg, 0.365 mmol.



 $^{1}\mathrm{H}$ NMR (400 MHz, Chloroform-d) δ 8.03 – 7.98 (m, 1H), 7.87 – 7.78 (m, 1H), 7.72 – 7.58 (m, 1H), 7.57 – 7.46 (m, 2H), 7.26 (s, 2H), 4.63 – 4.05 (m, 2H), 1.52 (s, 18H), 1.32 (s, 9H).

¹³C NMR (101 MHz, Chloroform-d) δ140.8, 139.2, 134.9, 133.6, 132.4, 130.1, 129.9, 129.1, 128.3, 121.9, 34.8, 34.4, 31.7, 30.3.

HRMS (EI): Calculated for $C_{25}H_{37}N = 352.0833$; found = 352.0831.

Yield of product 55: 65%; 114.1 mg, 0.325 mmol.



¹H NMR (400 MHz, Chloroform-d) δ 7.38–7.30 (m, 4H), 7.30–7.24 (m, 1H), 6.91–6.83 (m, 2H), 6.58–6.51 (m, 2H), 4.27 (s, 2H), 3.98 (bs, 1H).

¹³C NMR (101 MHz, Chloroform-d) δ 155.9, 144.4, 139.2, 128.71, 127.54, 127.36, 115.7, 113.7, 48.9.

 ^{19}F NMR (376 MHz, Chloroform-d) δ -127.78.

HRMS (EI): Calculated for $C_{13}H_{12}NF = 201.0948$; found = 201.0943.

Yield of product 56: 80%; 80.4 mg, 0.40 mmol.

¹H NMR (300 MHz, Chloroform-d) δ 7.30 – 7.19 (m, 5H), 7.07– 6.99 (m, 2H), 6.51– 6.43 (m, 2H), 4.22 (s, 2H), 4.76 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 146.5, 138.8, 129.1, 128.7, 127.5, 127.4, 122.2, 114.0, 48.4. HRMS (EI): Calculated for $C_{13}H_{12}NCl = 217.0652$; found = 217.0645.

Yield of product 57: 81%; 87.8 mg, 0.405 mmol.

¹H NMR (300 MHz, Chloroform-d) δ 7.24 – 7.04 (m, 4H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 8.9 Hz, 2H) 4.11 (s, 2H), 4.08 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-d) δ 162.1, 146.9, 134.6, 132.0, 129.0, 115.6, 114.5, 109.3, 47.5. ¹⁹F NMR (376 MHz, Chloroform-d) δ -122.23.

HRMS (EI): Calculated for $C_{13}H_{11}BrFN = 281.0146$; found = 281.0144.

Yield of product 58: 74%; 104 mg, 0.37 mmol.

¹H NMR (300 MHz, Chloroform-d) δ 7.26 – 7.22 (m, 2H), 7.16 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.06 – 6.96 (m, 4H), 6.69 (dq, *J* = 1.4, 0.7 Hz, 1H), 3.99 (s, 2H), 2.16 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 139.5, 134.8, 131.5, 128.9, 128.6, 127.6, 127.0, 126.4, 123.9, 117.8, 36.1, 21.5.

HRMS (EI): Calculated for $C_{14}H_{15}NO = 214.2803$; found = 214.0801.

Yield of product 59: 86%; 92.1 mg, 0.43 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.24 (d, J = 5.9, 2H), 7.20 – 7.13 (m, 2H), 6.84 – 6.75 (m, 2H), 6.65 – 6.57 (m, 2H), 4.20 (s, 2H), 3.72 (s, 3H), 3.60 (bs, 1H), 2.31 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.2, 142.6, 136.8, 136.7, 129.3, 127.6, 114.9, 114.1, 55.8, 49.0, 21.1.

HRMS (EI): Calculated for $C_{15}H_{17}NO = 228.2043$; found = 228.2041.

Yield of product 60: 85%; 96.9 mg, 0.425 mmol.



¹H NMR (300 MHz, Chloroform-d) δ 7.45 – 7.27 (m, 7H), 6.69 – 6.53 (m, 2H), 4.34 (s, 2H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 128.8, 127.5, 127.3, 126.6, 126.6, 112.0, 47.8. ¹⁹F NMR (282 MHz, Chloroform-d) δ -61.03. HRMS (EI): Calculated for $C_{15}H_{16}NF_3 = 268.0178$; found = 268.0176.

Yield of product 61: 80%; 107.1 mg, 0.40 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 5H), 6.56 – 6.50 (m, 2H), 6.42 – 6.38 (m, 1H), 4.33 (s, 2H), 3.85 (s, 3H), 3.77 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 152.1, 147.9, 139.8, 132.5, 128.5, 127.6, 127.1, 110.4, 103.7, 99.2, 55.8, 55.5, 48.8.

HRMS (ESI): Calculated for $C_{15}H_{17}NO_2$ [M+H] = 244.1337; found = 244.1337.

Yield of product 64: 78%; 95.2 mg, 0.39 mmol.



 1H NMR (300 MHz, Chloroform-d) δ 7.84 - 7.72 (m, 2H), 7.36 - 7.26 (m, 2H), 7.14 - 7.04 (m, 2H), 6.59 - 6.44 (m, 2H), 4.90 (bs, 1H), 4.30 (s, 2H), 3.80 (s, 3H),

¹³C NMR (75 MHz, Chloroform-d) δ 167.2, 150.9, 137.1, 131.8, 131.5, 129.1, 121.3, 119.4, 112.2, 51.7, 47.4.

HRMS (EI): Calculated for $C_{15}H_{14}BrNO_2 = 321.0134$; found = 321.0132.

Yield of product 65: 72%; 115.4 mg, 0.36 mmol.



¹H NMR (300 MHz, DMSO-d₆) δ 7.71 – 7.62 (m, 2H), 7.36 – 7.23 (m, 2H), 7.19 (bs, 1H), 6.73 – 6.57 (m, 2H), 4.46 (s, 2H), 3.73 (s, 3H).

¹³C NMR (75 MHz, DMSO-d6) δ 166.7, 152.5, 152.3, 149.0, 139.5, 137.7, 136.2, 131.3, 117.1, 111.9, 111.8, 111.7, 51.6, 45.7, 45.1, 8.8.

 ^{19}F NMR (282 MHz, Chloroform-d) δ -136.19, -165.50.

HRMS (EI): Calculated for $C_{15}H_{12}NO_2F_3 = 296.0817$; found = 296.0814.

Yield of product 66: 83%; 122.8 mg, 0.415 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 8.09 (m, 2H), 7.39 – 7.27 (m, 5H), 6.55 – 6.40 (m, 2H), 4.40 – 4.33 (m, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 153.6, 149.3, 137.8, 128.8, 127.6, 127.3, 107.7, 46.9. HRMS (ESI): Calculated for $C_{12}H_{12}N_2$ [M+H] = 185.1078; found =185.1074.

Yield of product 67: 86%; 79.5 mg, 0.43 mmol.



¹H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.31 (m, 5H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.22 – 6.16 (m, 2H), 4.26 (s, 2H), 4.24 – 4.20 (m, 2H), 4.20 – 4.15 (m, 2H), 3.66 (bs, 1H).

¹³C NMR (101 MHz, Chloroform-d) δ 144.1, 143.2, 139.5, 135.8, 128.6, 127.5, 127.2, 117.6, 106.8, 101.6, 64.7, 64.2, 49.1.

HRMS (ESI): Calculated for $C_{15}H_{15}NO_2$ [M+H] = 242.1181; found = 242.1181. Yield of product 68: 86%; 104.1 mg, 0.43 mmol.



1H NMR (400 MHz, Chloroform-d) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.44 – 7.30 (m, 6H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 6.69 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.50 (bs, 1H), 4.41 (s, 2H), 3.82 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.3, 145.2, 142.2, 142.2, 139.1, 132.3, 128.7, 127.6, 127.3, 126.6, 124.9, 124.7, 120.6, 118.5, 112.3, 109.5, 48.8, 36.9.

HRMS (ESI): Calculated for $C_{20}H_{17}N$ [M+H] = 270.1283; found = 270.1284.

Yield of product 69: 84%; 113.4 mg, 0.42 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.44 – 7.27 (m, 5H), 7.08 – 6.93 (m, 2H), 6.75 – 6.56 (m, 2H), 4.27 (s, 2H), 2.26 – 2.24 (m, 2H), 1.28 – 1.25 (m, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 149.0, 138.4, 133.4, 129.8, 128.6, 127.9, 127.4, 114.3, 49.5, 29.7, 20.5.

HRMS (EI): Calculated for $C_{15}H_{17}NO = 228.0412$; found = 228.0410.

Yield of product 70: 84%; 95.7 mg, 0.42 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.42- 7.24 (m, 10H), 3.82 (s, 4H), 1.61 (bs, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 140.5, 128.5, 128.3, 127.1, 53.3. HRMS (ESI): Calculated for C₁₄H₁₅N [M+H] = 198.1283; found = 198.1288. Yield of product 71: 81%; 80.2 mg, 0.405 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 3H), 7.15 – 7.07 (m, 2H), 6.52 – 6.44 (d, J = 2.3, 2H), 6.27 – 6.20 (t, J = 2.3, 1H), 3.68 – 3.63 (m, 6H), 3.46 – 3.38 (m, 4H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 161.0, 160.7, 142.3, 139.5, 128.7, 128.6, 128.3, 128.2, 126.9, 106.6, 106.6, 98.7, 58.0, 57.9, 55.4, 55.3.

HRMS (ESI): Calculated for $C_{16}H_{19}NO_2 = [M+H] 258.1494$; found = 258.1496. Yield of product 73: 79%; 101.9 mg, 0.395 mmol.

H N

¹H NMR (300 MHz, Chloroform-d) δ 7.50 – 7.24 (m, 10H), 3.89 (q, *J* =1.1, 6.6, 1H), 3.79 – 3.63 (m, 2H), 1.61 (bs, 1H), 1.45 (dd, *J* =1.1, 6.7, 3H).

¹³C NMR (75 MHz, Chloroform-d) δ 145.6, 140.7, 128.5, 128.4, 128.2, 127.0, 126.9, 126.7, 57.5, 51.7, 24.5.

HRMS (EI): Calculated for $C_{15}H_{17}N = 212.1078$; found = 212.1076.

Yield of product 74: 75%; 79.5 mg, 0.375 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 8.50 – 8.30 (m, 2H), 7.65 – 7.55 (dt, *J* =1.7, 7.8, 1H), 7.24 – 7.08 (m, 6H), 3.59 (s, 4H), 3.52 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 149.6, 148.4, 139.1, 136.2, 135.0, 128.5, 128.3, 127.3, 123.5, 52.9, 50.0.

HRMS (ESI): Calculated for $C_{13}H_{14}N_2$ [M+H] = 199.1235; found = 199.1237.

Yield of product 75: 82%; 81.6 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.18 – 7.12 (m, 5H), 7.12 – 7.07 (m, 2H), 7.07 – 7.02 (m, 3H), 3.67 (s, 2H), 2.80 – 2.73 (m, 2H), 2.72 – 2.65 (m, 2H), 1.87 (bs, 1H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 139.9, 139.9, 128.7, 128.5, 128.4, 128.2, 127.0, 126.2, 53.8, 50.4, 36.2.

HRMS (ESI): Calculated for $C_{15}H_{17}N$ [M+H] = 212.1439; found = 212.1444. Yield of product 76: 82%; 86.8 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.39 – 7.17 (m, 5H), 3.68 (s, 2H), 1.26 (bs, 1H), 1.12 (s, 9H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 141.4, 128.4, 128.3, 126.8, 50.7, 47.3, 29.1. HRMS (EI): Calculated for C₁₁H₁₇N = 164.1439; found = 164.1437.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.40 – 7.25 (m, 5H), 4.00 – 3.84 (d, J = 4.8, 2H), 3.31 – 3.06 (qd, J = 6.5, 9.4, 2H), 1.63 (bs, 1H). ¹³C NMR (75 MHz, Chloroform-d) δ 139.1, 128.5, 128.0, 127.4, 125.6, 53.0, 49.5. ¹⁹F NMR (376 MHz, Chloroform-d) δ -71.46. HRMS (ESI): Calculated for C₁₀H₁₄NF₃ [M+H] = 206.0491; found = 206.0488.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.10 (m, 5H), 3.83 – 3.65 (m, 2H), 3.18 (bs, 1H), 2.51 – 2.50 (m, 2H), 1.42 – 1.07 (m, 6H), 0.82 – 0.77 (m, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 139.0, 127.7, 127.4, 127.3, 127.0, 126.1, 57.2, 47.9, 28.4, 21.5, 12.9.

HRMS (ESI): Calculated for $C_{12}H_{19}N$ [M+H] 178.1595; found = 178.1591. Yield of product 80: 82%; 73.0 mg, 0.41 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 5H), 4.03 (bs, 1H), 3.80 – 3.61 (m, 2H), 2.73 – 2.39 (m, 2H), 1.64 – 1.51 (m, 2H), 1.37 – 1.18 (m, 12H), 0.92 – 0.88 (m, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 137.6, 126.3, 126.1, 126.0, 125.6, 124.8, 50.9, 46.4, 29.4, 29.4, 27.0, 27.0, 26.8, 24.8, 20.2, 20.2, 11.6.

HRMS (ESI): Calculated for $C_{14}H_{23}N$ [M+H] = 206.1908; found = 206.1913. Yield of product 81: 86%; 88.4 mg, 0.43 mmol.

¹H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.12 (m, 5H), 6.90 – 6.83 (m, 2H), 6.50 – 6.39 (m, 2H), 4.38 (s, 2H), 3.27 (td, *J* = 5.3, 1.9 Hz, 2H), 2.72 (t, *J* = 6.3 Hz, 2H), 1.92 (dtdd, *J* = 7.0, 5.9, 4.2, 1.1 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-d) δ 145.69, 139.03, 129.08, 128.65, 127.26, 126.83, 126.66, 122.29, 115.92, 111.04, 55.26, 49.97, 28.31, 22.46.

HRMS (ESI): Calculated for $C_{17}H_{17}N$ [M+H] = 224.1439; found = 224.1443.

Yield of product 82: 80%; 89.5 mg, 0.40 mmol.

¹H NMR (300 MHz, Chloroform-*d*) δ 7.25 – 7.04 (m, 2H), 6.73 – 6.45 (m, 3H), 3.71 (bs, 1H), 2.72 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 149.3, 129.2, 117.3, 112.4, 30.7.

HRMS (EI): Calculated for $C_7H_9N = 108.1412$; found =108.1410.



¹H NMR (300 MHz, Chloroform-d) δ 7.21 – 7.05 (dq, *J*=4.3, 5.8, 8.7, 1H), 6.76 – 6.33 (dt, *J*=4.1, 33.3, 3H), 3.60 (bs, 1H), 2.88 (s, 3H), 2.38 (s, 3H). ¹³C NMR (75 MHz, Chloroform-d) δ 149.4, 139.0, 129.1, 118.2, 113.2, 109.7, 30.8, 21.6. HRMS (EI): Calculated for C₈H₁₁N = 122.0914; found =122.0912. Yield of product 86: 61%; 37.2 mg, 0.305 mmol.



¹H NMR (400 MHz, DMSO-*d*₆) δ 7.15 – 6.86 (m, 2H), 6.74 – 6.46 (m, 2H), 5.53 (bs, 1H), 2.81 – 2.65 (m, 3H).

¹³C NMR (101 MHz, DMSO- d_6) δ 151.3 (d, J = 237.4 Hz), 138.4 (d, J = 11.8 Hz), 125.2 (d, J = 3.5 Hz), 115.4 (d, J = 6.7 Hz), 114.4 (d, J = 17.9 Hz), 111.6 (d, J = 4.1 Hz), 29.9.

¹⁹F NMR (376 MHz, DMSO-d6) δ -135.65.

HRMS (EI): Calculated for $C_7H_8NF = 126.0615$; found = 126.0613.

Yield of product 87: 56%; 35.2 mg, 0.28 mmol.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 7.11 (m, 2H), 6.55 – 6.50 (m, 2H), 3.68 (bs, 1H), 2.81 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 147.8, 129.0, 121.8, 113.4, 30.8.

HRMS: Calculated for $C_7H_8NC1 [M+H] = 142.0423$; found = 142.0424.

Yield of product 88: 41%; 29.1 mg, 0.205 mmol.



 $^1\mathrm{H}$ NMR (300 MHz, Chloroform-d) δ 7.51 – 7.41 (m, 1H), 7.29 – 7.17 (s, 1H), 6.73 – 6.56 (m, 2H), 4.36 (bs, 1H), 2.91 (s, 3H).

¹³C NMR (75 MHz, Chloroform-d) δ 145.9, 132.3, 128.5, 117.6, 110.8, 109.6, 30.6.

HRMS (EI): Calculated for $C_7H_8NBr = 184.9834$; found = 184.9828.



¹H NMR (300 MHz, Chloroform-*d*) δ 7.46 – 7.38 (m, 2H), 6.64 – 6.57 (m, 2H), 4.06 (bs, 1H), 2.87 (s, 3H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 151.6, 126.8, 126.64, 126.5, 126.5, 126.4, 123.2, 118.8, 118.4, 111.4, 30.2.

 19 F NMR (376 MHz, Chloroform-d) δ -60.92.

HRMS (EI): Calculated for $C_8H_8NF_3 = 176.0114$; found = 176.0112.

Yield of product 90: 57%; 50.1 mg, 0.285 mmol.



¹H NMR (300 MHz, Chloroform-*d*) δ 6.84 – 6.77 (m, 2H), 6.63 – 6.57 (m, 2H), 3.76 (s, 3H), 3.42 (bs, 1H), 2.82 (s, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 152.1, 143.6, 114.9, 113.7, 55.8, 31.6. HRMS (EI): Calculated for C₈H₁₁NO = 137.0835; found = 137.0832. Yield of product 91: 60%; 41.1 mg, 0.30 mmol.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (ddd, J = 8.1, 2.2, 0.9 Hz, 1H), 7.27 (t, J = 8.1 Hz, 1H), 6.87 (ddd, J = 8.2, 2.4, 0.9 Hz, 1H), 4.17 (s, 1H), 2.90 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 149.9, 149.4, 129.6, 118.5, 111.8, 105.8, 30.5. HRMS (EI): Calculated for C₇H₈N₂O₂ = 153.0217; found = 153.0214.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.30 (m, 2H), 6.60 – 6.36 (m, 2H), 4.24 (bs, 1H), 2.76 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 152.1, 133.6, 120.5, 111.9, 98.6, 30.0.

HRMS (EI): Calculated for $C_8H_8N_2 = 132.0603$; found = 132.0601.



¹H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 7.70 (dq, *J* =2.1, 4.6, 1H), 7.48 – 7.14 (s, 1H), 6.56 – 6.12 (m, 2H), 5.08 (bs, 1H), 2.97 – 2.59 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.7, 147.9, 137.3, 112.4, 106.2, 28.9. HRMS (ESI): Calculated for C₆H₈N₂ [M+H] = 109.0765; found = 109.0768. Yield of product 94: 60%; 32.7 mg, 0.30 mmol.

NH₃+Cl

¹H NMR (300 MHz, DMSO- d_6) δ 9.97 – 8.20 (m, 3H), 8.18 – 8.14 (m, 1H), 8.02 – 7.96 (m, 2H), 7.72 – 7.69 (dd, J =1.2, 7.1, 1H), 7.63 – 7.5 (m, 3H), 4.49 (s, 2H).

¹³C NMR (75 MHz, DMSO-*d*₆) δ 133.6, 131.1, 130.9, 129.3, 129.0, 127.5, 127.1, 126.6, 125.8, 123.9, 39.7.

Yield of product 97: 59%; 113.8 mg.

F ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.45 – 7.22 (dd, *J* = 5.6, 8.3, 2H), 7.20 – 6.99 (m, 2H), 3.71 (s, 2H), 1.78 (bs, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 161.3 (d, *J* = 241.0 Hz), 140.9 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 7.9 Hz), 115.1 (d, *J* = 21.0 Hz), 45.3. ¹⁹F NMR (376 MHz, DMSO-d6) δ -117.32. Yield of product 98: 62%; 77.5 mg.

CI NH3⁺CI-

NH₂

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.66 (s, 3H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.5 Hz, 2H),
3.91 (s, 2H).
¹³C NMR (101 MHz, DMSO-*d*₆) δ 131.6, 131.5, 129.5, 126.9, 39.9.
Yield of product 99: 69%; 122.1 mg.



¹H NMR (400 MHz, DMSO-*d*₆) δ 9.03 – 8.68 (s, 3H), 7.68 – 7.63 (m, 1H), 7.49 – 7.45 (m, 1H), 7.39 – 7.34 (m, 2H), 4.05 (s, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 131.9, 130.7, 129.7, 129.3, 128.5, 126.5, 38.4.

Yield of product 100: 65%; 114.7 mg.



¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.1, 2H), 7.40 (d, *J* = 8.3, 2H), 3.84 (s, 2H), 1.51 (bs, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.1, 129.0 (q, *J* = 32.2 Hz), 127.2, 125.3 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 273.71 Hz), 45.9.

 ^{19}F NMR (376 MHz, Chloroform-d) δ -62.39.

Yield of product 101: 60%; 105 mg.

NH₂

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (t, *J* = 7.8, 1H), 6.91 – 6.84 (m, 2H), 6.80 – 6.75 (ddd, *J* = 1.0, 2.6, 8.3, 1H), 3.83 (s, 2H), 3.80 (s, 3H), 1.56 (bs, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 145.0, 129.6, 119.3, 112.2, 55.2, 46.4.

Yield of product 102: 72%; 98.6 mg.



¹H NMR (400 MHz, DMSO- d_6) δ 8.65 (s, 3H), 7.41 – 7.32 (m, 5H), 7.32 – 7.27 (d, J = 7.5, 2H), 6.99 – 6.90 (d, J = 8.0, 2H), 5.03 (s, 2H), 3.76 (s, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 158.6, 137.3, 131.0, 128.8, 128.2, 128.0, 126.6, 115.2, 69.6, 42.0. Yield of product 104: 60%; 149.1 mg.

¹H NMR (300 MHz, DMSO- d_6) δ 8.80 (s, 3H), 7.97 – 7.88 (dd, J = 1.5, 8.3, 2H), 7.79 – 7.70 (dd, J = 1.6, 8.3, 2H), 4.11 (s, 2H). ¹³C NMR (75 MHz, DMSO- d_6) δ 140.1, 132.8, 130.3, 119.0, 111.5, 42.0.

Yield of product 105: 31%; 52.1 mg.

NH₂

¹H NMR (300 MHz, Chloroform-*d*) δ 8.35 – 8.19 (dtd, J = 1.5, 3.0, 4.9, 1H), 7.44 – 7.28 (tdd, J = 1.7, 3.4, 7.3, 1H), 7.06 – 6.96 (dt, J = 2.5, 8.1, 1H), 6.92 – 6.80 (m, 1H), 3.71 – 3.66 (m, 2H), 1.60 (bs, 2H).

¹³C NMR (75 MHz, Chloroform-*d*) δ 161.8, 149.0, 136.2, 121.5, 120.9, 47.6.

Yield of product 106: 70%; 75.6 mg.



¹H NMR (400 MHz, DMSO- d_6) δ 8.83 (s, 3H), 7.28 – 7.08 (d, J = 3.9, 1H), 7.06 – 6.81 (m, 2H), 6.09 – 5.90 (s, 2H), 4.07 – 3.77 (m, 2H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 147.6, 128.1, 123.3, 110.0, 108.6, 101.6, 42.3.

Yield of product 108: 62%; 117.1 mg.

S7. NMR spectra



270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)












20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)







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10 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

-167.15



211115.314.10.fid Zhuang Ma ZM 4-460 Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2111 14



120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)





140.46 130.72 120.33 129.33 129.32 129.31 129.11 124.19 124.19 124.19 124.19 124.19 118.22 118.22 118.22

200427.411.11.fid Zhuang Ma ZM 4-89 Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 2004 11





211115.311.10.fid Zhuang Ma ZM 4-89 Au19F CDCl3 {C:\Bruker\TopSpin3.6.2} 2111 11



120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)



200429.f339.10.fid Zhuang Ma ZM 4-78 PROTON CDCI3 {C:\Bruker\TopSpin3.6.0} 2004 39



200619.f315.11.fid Zhuang Ma ZM4-151 H1CPD CDCI3 {C:\Bruker\TopSpin3.6.0} 2006 15



200619.f315.11.fid

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210322.f363.10.fid Zhuang Ma / zm4-234 PROTON CDCI3 {C:\Bruker\TopSpin3.6.2} 2103 3













129.42 127.76 123.91 118.32 113.02

 $\underbrace{ \underbrace{}_{147.47}^{147.47} }_{147.20}$







- 77.50 CDCl3 - 77.08 CDCl3 - 76.65 CDCl3

















270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



































270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm) 200603.f360.10.fid Zhuang Ma ZM4-167 PROTON CDCI3 {C:\Bruker\TopSpin3.6.0} 2006 60




















































210421.428.11.fid Zhuang Ma, ZM 4-108 Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 2104 28



210423.447.10.fid Zhuang Ma ZM4-108 F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2104 47



										-			120	100		150	1.00	170	100	100		
10	0	-10	-20	-30	-40	-50	-60	-70	-80	-90	-100	-110	-120	-130	-140	-150	-160	-1/0	-180	-190	-200	-210
	f1 (ppm)																					



210511.329.10.fid Ma/ ZM4-18 Au1H CDCl3 {C:\Bruker\TopSpin3.6.2} 2105 29





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 fl (ppm)

200525.f333.11.fid Zuhang Ma ZM4-184-2 H1CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 2005 33













120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)









120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 f1 (ppm)

200527.338.11.fid Zhuang Ma ZM 4-190 Au1H CDCI3 {C:\Bruker\TopSpin3.6.0} 2005 38



























210617.319.10.fid Zhuang Ma ZM4-469 Au1H CDCI3 {C:\Bruker\TopSpin3.6.2} 2106 19








210423.444.10.fid Zhuang Ma ZM4-199 F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2104 44

F H F



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



























210520.415.12.fid Ma/ ZM4-316 F19 DMSO {C:\Bruker\TopSpin3.5pl6} 2105 15



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)









270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

210615.434.10.fid Zhuang Ma ZM4-312 F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2106 34

F CH₃

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



















210520.416.12.fid Ma/ ZM4-410 F19 DMSO {C:\Bruker\TopSpin3.5pl6} 2105 16



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)











210423.445.10.fid Zhuang Ma ZM4-405 F19 CDCl3 {C:\Bruker\TopSpin3.5pl6} 2104 45



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)















